Sustainability and Ecolabels: Re-thinking the Anaerobic Biodegradation Criterion for Linear Alkylbenzene Sulfonate (LAS)

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Summary (Abstract)

Limitations on anaerobically nonbiodegradable (anNBO) surfactants and on total anNBO substances in laundry and cleaning products are criteria in the EU and other European ecolabel programs. The justification for these criteria is that these reduce the concentration of anNBO substances in the environment, specifically in the sludge output from anaerobic digesters of wastewater treatment plants (WWTPs). Is that sufficient justification in itself or are there also sustainability or other benefits to the environment?

This question is examined using linear alkylbenzene sulfonate (LAS) as a test case. LAS is the largest volume, best studied surfactant that does not meet the strict requirements for anaerobic biodegradation in the EU ecolabel program (>60% complete biodegradation (mineralization) within 60 days in standard anaerobic biodegradation screening tests).

Abstract (part 2):

The available data demonstrate:

1) Current LAS uses do not pose a risk to the aquatic environment, sediment or soil, compartments potentially impacted by anNBO substances. This is true even for worst case (direct discharge) situations.

2) LAS, which is rapidly and completely biodegraded under aerobic conditions, does not accumulate in the environment since environmental compartments receiving LAS (rivers and streams, sediments and soil) are primarily aerobic.

3) Recent studies demonstrate LAS biodegrades in environmental compartments that are not aerobic, including microaerophilic conditions, anaerobic marine sediments with low organic content, and anaerobic bioreactors, vessels intended to facilitate wastewater treatment.

Abstract (part 3)

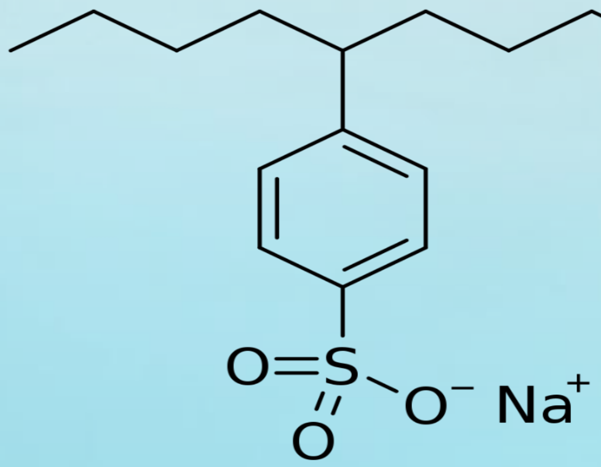
Conclusion:

The available data do not support a finding that anaerobic biodegradation criterion contribute to sustainability or provide other benefits to the environment. On the contrary, the data suggest that justification for anNBO criteria needs to be re-examined.

Outline of presentation

- Introduction on:
  - LAS (linear alkylbenzene sulfonate)
  - Anaerobic biodegradation
  - Ecolabel programs
- Main focus: Potential benefits of anaerobic biodegradation criteria, identified as:
  - Reduced risk/increased safety
  - Reduced waste
  - Increased sustainability
- Conclusions and further resources, including literature cited.

Information on LAS structure and use



This is the LAS molecular structure, showing the C12 alkyl chain homologue. Commercial LAS consists of a mixture of C10 to C13 alkyl chains, each attached to the phenyl group at any of the non-terminal positions; the sulfonate group is attached at the para position on the phenyl ring.

- LAS is a major surfactant used in laundry detergents and cleaning products worldwide.
- Its environmental properties have been, and continue to be, extensively studied.
- The REACH assessment of LAS is available on-line. It shows:
  - All Risk Characterization Ratio (RCR) values are less than 1,
  - Indicating risks are controlled, and
  - No additional risk management required.

Anaerobic biodegradation compared with aerobic biodegradation

- **“Anaerobic biodegradation” is biodegradation in the absence of oxygen (anoxic conditions)**
- **“Aerobic biodegradation” is biodegradation in the presence of oxygen (oxic conditions)**
- **Waste substances typically pass through oxic conditions before reaching anoxic compartments. For instance-**
  - **anaerobic digesters of wastewater treatment plants (WWTPs) are anaerobic but biological treatment, which proceeds sludge digestion, is oxic**
  - **Deep sediments are anaerobic but surface water and sediments are oxic.**
- **Aerobic biodegradability is a key parameter in risk assessments (such as REACH) but anaerobic biodegradability is not.**

Logos of the Ecolabel programs considered:

EU Flower

German Blue Angel

Nordic Swan

Ecolabel programs

- Intended to identify environmentally superior products using agreed criteria. For laundry detergents and cleaning products, these include requirements for anaerobic biodegradability -
- For the EU Flower:
  - Surfactants must demonstrate greater than 60% mineralization within 60 days using screening tests such as the ECETOC 28 test, or higher tier simulation tests.
    - This criterion applies to surfactants classified for aquatic toxicity as Acute Cat. 1 (LC50/EC50/ErC50 values greater than or equal to 1 mg/L) or Chronic Category 3, having a NOEC between 0.1 and 1 mg/L; LAS is Chronic category 3.
  - There is also a limit on total organic substances that are anaerobically non-biodegradable, abbreviated as anNBO.
- For the German Blue Angel and Nordic Swan, all surfactants must meet anaerobic biodegradability criterion (ECETOC 28 test or equivalent)

Key question: Is there science-based justification for restrictions on anNBO substances?

- LAS is examined as a test case because it is the largest volume, best studied surfactant that does not meet the requirements for anaerobic biodegradation in ecolabel programs.
- Because of structural similarities among surfactants, the conclusions on LAS likely apply to other anNBO substances, including:

  alkyl sulfonates
  dialkyl sulpho succinates
  sulpho fatty acid methylesters
  alfa olefin sulphonates
  C12-18 alcohol ethoxylates

Potential justifications considered:

1. Reduced risk/increased safety (5 worst case environmental compartments considered)

2. Reduced waste to the environment (2 environmental compartments considered)

3. Increase sustainability

Potential benefit #1: Reduced risk/increased safety

Safety assessments indicate current uses of LAS do not pose an unacceptable risk to environmental compartments, meaning LAS poses low risk. Worst case examples considered:

1. **For the terrestrial environment, sludge-amended soil in which sludge from a WWTP anaerobic digester is use as a fertilizer or soil conditioner.**
2. **For aquatic environments that are potentially anoxic and low oxygen**
   A. **Freshwater receiving effluent dominated WWTP discharges**
   B. **Freshwater receiving primary discharges**
   C. **Marine outfalls**
   D. **Subsurface sediments, whether freshwater or marine**

Worst case #1: Soil amended with anaerobic digester sludge

- The LAS soil PNEC value is 35 mg/kg dry weight
  - This value is well documented, based on studies on food crops and other plants as well as soil microorganisms, earthworms and other soil macro organisms.
- Key finding: LAS levels in sludge-amended soil are below the soil PNEC
  - LAS levels are about 1 mg/kg dw at harvest.
- <u>Conclusion</u>: LAS in anaerobic digester sludge poses low (acceptable) risk to the terrestrial environment.

Worst case #2: Freshwater receiving effluent dominated WWTP discharges

- Studies in the US have searched for links between concentrations of effluent components and ecological impacts in effluent-dominated rivers.
- The most sensitive endpoints were reduced community diversity, either in fish and/or macroinvertebrates.
- Key finding: The effluent factors responsible were ammonia, metals and/or low dissolved oxygen, not surfactant concentrations.

Worst case #3: Freshwater receiving primary discharges

- In a case study in the Balatuin River, the Philippines (near the city of San Pablo), direct discharge of domestic effluents produced a “dead zone” with no fish or invertebrates in the river water.
- Ecological recovery was observed downstream, due to microbial activity and natural aeration of river water.
- Critical factors for recovery were:
  - Reducing high biochemical oxygen demand (BOD) levels
  - Restoration of adequate dissolved oxygen levels
  - Degradation of excess ammonia.
- Key finding: LAS biodegraded faster than BOD and thus was <u>not</u> a critical factor in river recovery.

Worst case #4: Marine outfalls

- LAS levels in coastal water and sediments are below PNEC values for aquatic and sediment organisms, indicating low risk.
- Exceptions are receiving zones in the immediate vicinity of WWTP outfalls.
- Data on effluent dominated and direct discharges – just discussed - suggest ecological impacts in receiving zones unlikely to be due to surfactants/detergent ingredients.

Worst case #5: Subsurface sediments

- Environmental fate studies indicate LAS may be present in subsurface sediments, including freshwater and marine coastal and estuary sediments.
- WWTP effluent solids are the likely source of LAS, as LAS, like other surfactants, strongly sorbs to solids.
- Key point: Limited fauna are present in anaerobic sediments, typically anaerobic/facultative microorganisms.
- LAS levels are below microbial NOECs, indicating low risk.

Conclusions on Reducing risk/increasing safety

- LAS poses low risk even to worst case terrestrial or aquatic/sediment environments.
- No data available indicating that restricting LAS use improves environmental safety.
- No risk/safety benefit identified for anNBO restrictions.

Potential benefit #2: Reducing waste in the environment

- The stated justification for anNBO restrictions is that these reduce the concentration of anNBO substances in the environment.
- Prime focus is sludge output from anaerobic digesters of WWTPs.
- Other anoxic environmental compartments also will be considered.

Reducing waste case #1: Anaerobic digester sludge

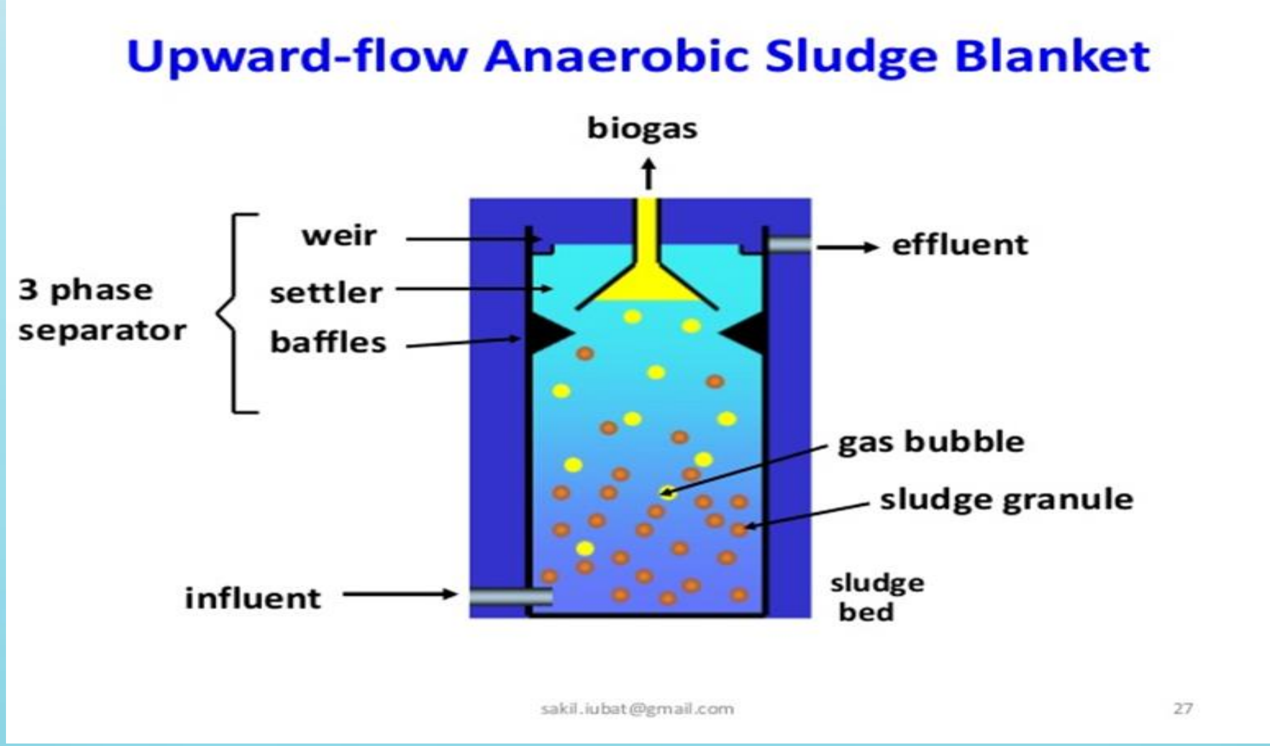
- **The Environmentally preferred mode of sludge disposal is use as soil fertilizer or conditioner (sludge amended soil).**
- **Data demonstrate:**
  - **Even for anaerobic digester sludge, LAS biodegradation resumes once sludge is exposed to air, which may occur during shipment and storage, even before sludge is applied to soil.**
  - **Rapid rates of LAS biodegradation** are **observed in sludge amended soil, with half-lives of 7-22 days.**
  - **Rapid biodegradation prevents build up of LAS in soil receiving multiple applications of sludge.**
- **Alternative sludge disposal methods are incineration and land filling.**
- There is **No evidence that restricting anNBO substances, regardless of the sludge disposal method, results in lower cost/improved disposal.**

Reducing waste case #2: Other anoxic environmental compartments

LAS anaerobic biodegradation recently demonstrated in -

- **Sulfate limited conditions (observed in certain soils)**
- **Marine sediments, where**
  - **The initial steps of biodegradation are the same as the established mechanism for long-chain alkanes.**
  - **The similarity of the initial biodegradation steps is understandable since LAS may be considered a long-chain (C10-C13) alkane with a sulfo phenyl group attached.**
- **Anaerobic bioreactors, vessels optimized for wastewater treatment.**

Schematic of a commonly used bioreactor, an up-flow anaerobic sludge blanket reactor. In this reactor, influent flows into the bottom of the vessel, effluent flows out the top and biogas is collected via a phase separator; sludge granules, where biodegradation takes place, are retained by gravity settling.



Bioreactor studies

LAS anaerobic biodegradation has been well documented (over 30 studies)

- **Bioreactors are useful for treatment of laundry wastewater, with optimal removal rates of 50% biodegradation with a 36 hour hydraulic residence time (HRT) at 30 °C.**
  - **More efficient than anaerobic digesters with 7-14 day HRTs and no measurable LAS degradation.**
  - **Difference in efficiency likely due digesting sludge (with high organic content) versus treating laundry wastewater with LAS as the major carbon source.**

Bioreactors – Key findings

- **LAS anaerobic biodegradation occurs in bioreactors using a variety of sludge sources, including anaerobic digester sludge.**
- **Demonstrates anaerobic digester sludge has the potential to anaerobically biodegrade LAS.**
- **Raise the question of whether LAS should be considered anNBO.**
- **Suggest that anNBO criteria (reliance on the ECETOC 28 and related tests) need to be re-examined as anNBO substances <u>can</u> anaerobically biodegrade in relevant environmental compartments.**

Conclusion on Reducing waste

- Waste-reduction benefits are not obvious from consideration of sludge-amended soil and demonstration of LAS anaerobic biodegradation in polluted rivers, soils, marine sediments and bioreactors.

Potential benefit #3: Increased sustainability

- The United Nations defines sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs.
- For ecolabel programs, the only criteria identified as directly related to sustainability are those for “Sustainable sourcing of palm oil, palm kernel oil and their derivatives.”
- Restricting anNBO use has no identifiable benefit for sustainability.

Conclusions on Sustainability

- Sustainability is such an important goal that it is surprising that the only ecolabel criteria directly related to sustainability are for palm and palm kernel oil sourcing.
- Ecolabel criteria such as anNBO restrictions do not support the goal of sustainability because these restrictions, as discussed above:
  - Do not reduce risk or increase safety, and
  - Do not reduce waste.

Overall conclusions

- The available data do not support a finding that anaerobic biodegradation criteria contribute to sustainability, reduce waste or increase environmental safety.
- The justification for restrictions on anNBO substances in ecolabel programs needs to be re-examined.
- More work needs to be done on ecolabel criteria to:
  - Better explain how the criteria relate to sustainability
  - Increase the number of criteria that relate to this important goal.

Further Resources

Further information on LAS and CLER is available at:

- The CLER website (https://cler.com)
- The CLER LinkedIn webpage (https://www.linkedin.com/company/the-council-for-lab-las-environmental-research/)
- Literature cited (next pages)

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